SLAGGING BEHAVIOUR OF WOOD ASH UPON ENTRAINED-FLOW GASIFICATION CONDITIONS: PRELIMINARY STUDIES

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Introduction

Entrained flow gasification is one of the most promising technologies to convert biomass streams for large-scale applications aimed at (integrated) production of power, hydrogen and chemicals (e.g. Fischer-Tropsch diesel fuels). Application of biomass streams in entrained-flow gasifiers similar to those employed in coal gasification (e.g. slagging gasifiers) requires R&D concerning fuel feeding and ash behavior, especially with regard to ash slagging tendencies.

This paper present results related to characterization of slag behaviour of selected wood streams - beech, willow, wood mixture - under simulated (pressurized, oxygen blown) entrained-flow gasification conditions. Wood ash in the fuel is very low (about 1% fuel weight), and characterized by high alkaline-earth and alkali metals content. Therefore its application upon conditions typical of slagging gasifiers requires careful adaptation, since the latter are designed for higher fuel ash content (typically > 6% fuel weight) and operate at a temperature where coal ash can form a molten slag (typically 1300-1500 °C).

Methods

The approach is based on experimental and modeling work. Experiments were performed in an atmospheric-pressure entrained-flow reactor, equipped with an integrated, premixed and multi-stage flat flame gas burner[1]. A scheme of the reactor is shown in **Figure 1**.

The ring-shaped, concentric, staged gas burner is used to simulate the (high) initial heating rates, and serves as a source for the reaction atmosphere. The alumina reactor, placed in a two-stage electrically-heated furnace, is designed to mimic the temperature-time history that coal/biomass/char particles experience in entrained-flow gasifiers. The flamefront temperature can be set as high as 2600 °C, while the reactor/furnace can withstand 1750 °C. The residence times possible to achieve in the system are a couple of hundreds milliseconds scale, allowing for high degrees of conversion of biomass fuels. The slagging behavior of the ash has been characterized by means of a deposition probe, on which top an alumina plate was placed, kept uncooled. The probe was set axially at different positions along the reactor, thus simulating different particle residence times. For this experimental campaign, the reactor furnace temperature was set at 1450 °C, while flame temperature has reached approx. 2050 °C (see **Figure 2**).

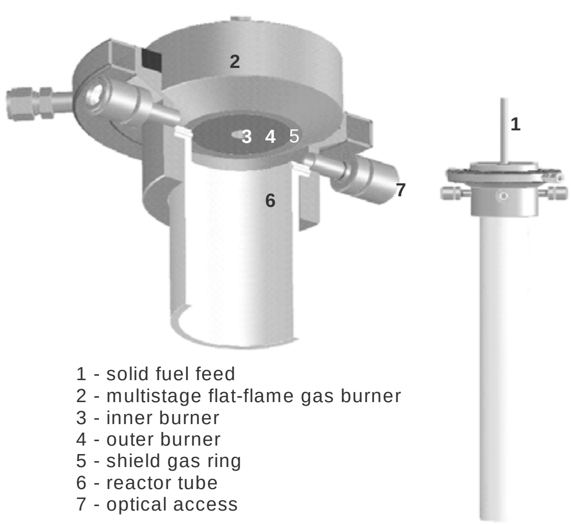

Figure 1. Schematic of the LCS test rig

SEM/EDX techniques have been applied to characterize the slag sample obtained. In addition, knowledge on slagging/melting tendencies of the selected fuels has been studied using an equilibrium model (FACTSAGE computer model) minimizing Gibbs free energy of an hypothetical (pressurized) entrained-flow gasification system, as well as simulating operation conditions close to the experimental ones.

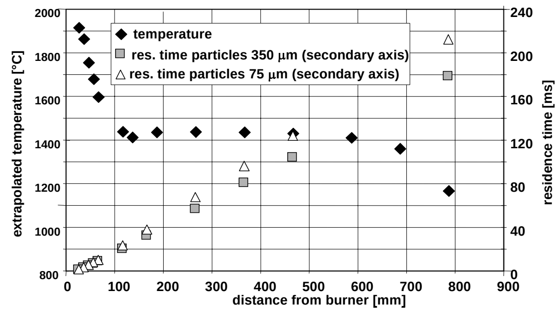

Figure 2. Experimental Temperature/Residence Time Profiles

Fuels. Experiments have been performed with three different woods: beech, willow, and a mixed wood that is commonly utilized in a Dutch power station. Fuel ash composition is shown in **Table 1**.

	beech	willow	wood mixture
Ash content (wt%)	1.01	1.9	1.51
Cl (wt% daf)	0.0037	0.02	0.19
S (wt% daf)	0.017	0.057	0.4
Si (mg/kg fuel)	171	618	417
Al (mg/kg fuel)	48	60	94
P (mg/kg fuel)	89	708	192
Mg(mg/kg fuel)	366	524	252
K(mg/kg fuel)	1151	2894	974
Ca(mg/kg fuel)	3096	5720	2417
Fe (mg/kg fuel)	47	68	116
Na(mg/kg fuel)	8	210	53

Table 1. Fuel Ash Content and Fuel Ash Composition

Results and Discussion

The results of the experimental campaign have shown that wood ash is not prone to form a fluid slag at typical operating temperatures of slagging gasifiers (e.g. 1300-1500 °C). **Figure 3** shows a SEM picture of a particle of beech ash slag after an experiment of 2 hrs. duration time. On the top of the deposit probe no uniform melt/ash layer was found, but rather single (clusters of) ash particles in which the original wood particle structure is still recognizable. Shifting the deposit probe position from 300 to 760 mm (corresponding to changing the residence time from 80 to 220 ms) does not improve the melting behavior of the ash. Only a small share of particles undergoes an enhanced melt formation due to formation of a Ca-silicate structure.

The results of the experimental campaign were well correlating with the predictions of the FACT-SAGE thermodynamic equilibrium program in terms of molten slag composition, which predict that overall at 1400 °C only 17% of the total ash-forming constituents in the wood will form a molten slag. Condensation of CaO is predicted to begin in the temperature window 1800-1700 °C. At 1000 °C, 74% of the total Ca in the fuel will form condensed CaO. Alkalis will exclusively form gaseous species overall the temperature range 2000-1000 °C, over a wide pressure range 5-30 bars. The experimental results were similar for the three types of wood ash investigated. For willow, it has been experimentally found out that the higher fuel phosphor content might partly enhance the melting behavior of the slag. **Figure 4** shows a typical (cluster of) particles upon gasification of willow: a molten slag structure, phosphor-enriched, is recognizable, whereas the non-molten structure is composed predominantly by CaO.

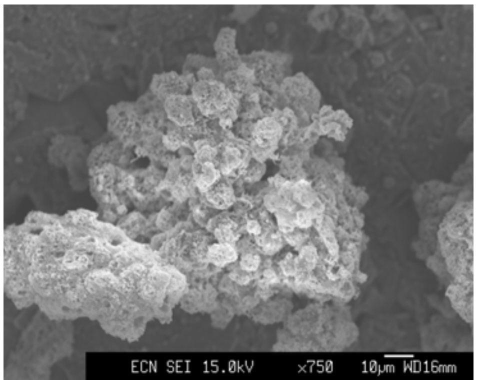

Figure 3: Micrograph of a beech gasification slag deposit

Changing the material substrate of the deposit probe plate was seen not to influence the melting behavior of the ash; on the contrary, wood ash particles have been homogeneously encapsulated in the melt when a pre-existing melt on the deposit probe-plate was present.

Since the wood ashes are not prone to melt under typical operating process temperatures of entrained flow slagging gasifiers, additives will be required which will lower the melting point of the ash.

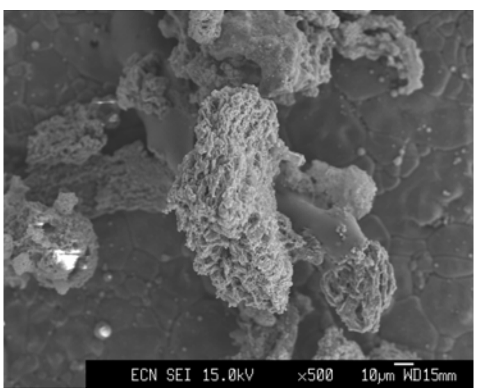

Figure 4: Micrograph of a willow gasification slag deposit

In this respect, additives rich in quartz or clay may enhance the overall fluidity of the slag. Experiments performed with beech wood mixed with SiO_2, (~99% purity), in agreement with thermodynamic calculations and with standard ash fusion test (DIN 51730), have shown that adding quartz on a molar ratio Si: Ca_{fuel} = 1:1; 2:1 (correspondent to 600 g – 1200 g quartz/kg fuel ash) may be sufficient to decrease the melting point of the ash system down to typical process operating temperatures.

Under experimental conditions, a layer of molten slag, (Ca-Silicate) was found on the deposit probe plate. When adding quartz, alkaline earth (and, to a less extent, alkali) metals will tend to be encapsulated in the silicon-based melt. Clay compounds have been predicted by thermodynamic calculations to perform in a similar way as SiO_2 in terms of increasing the total molten slag amount in the system.

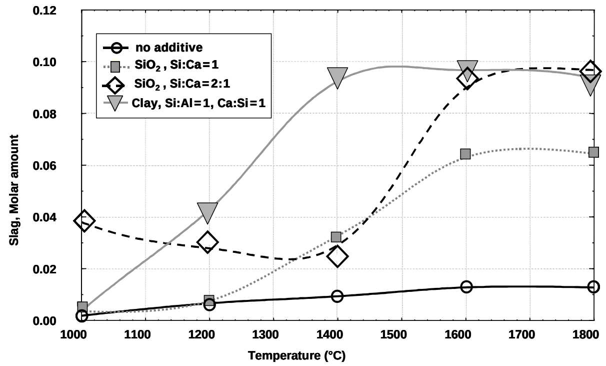

Figure 5: Influence of different additives on slag amount

Figure 5 shows the results of the thermodynamic equilibrium predictions plotting the molten slag amount versus temperature.

When adding a clay with a share of Al: Si=1:1 and Si: Ca_{fuel}=1:1 molar ratio), 90% of the total ash forming constituents will constitute a liquid melt at 1400 °C, according to thermodynamic predictions. This is due to the fact that Ca will be effectively encapsulated in the Al/Si based matrix.

Application of empirical viscosity models, such as Urbain-Kalmanovitch[2], to the investigated optimal wood/flux mixtures, show that viscosity may reach values in the range 8-15 Pa*s, thus achieving both sufficient fluidity to allow free flow and easy slag tapping is possible over typical temperature conditions. However, availability of data on slag flow properties in the composition range of wood ash with flux streams is limited[3], and more work is needed to assess quantitatively the characteristics of the slag flow in terms of viscosity versus slag composition and temperature.

Conclusions

Wood ash is not prone to form a fluid molten slag at typical operating conditions of (pressurized, oxygen-blown) entrained-flow gasifiers due to the formation of high-temperature melting compounds (e.g. CaO). Flux addition with quartz-based or clay-based compounds is a promising option to improve slag behavior by reducing the melting point of the slag. Further work is required to assess quantitatively the characteristics of the slag flow, especially in terms of viscosity versus slag composition and temperature.

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